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(54) **Oxidation of carbon monoxide and catalyst therefor.**

(57) A composition of matter comprising titania and Pt and/or Pd is prepared by a process comprising one step of heating Pt and/or Pd-impregnated titania with a reducing gas, in particular free hydrogen, at a temperature of about 300-800 °C. Another composition of matter comprising titania and Pt and/or Pd is prepared by a process comprising the steps of coating a porous ceramic material (preferably a monolith) with colloidal TiO₂, drying, impregnation with Pt and/or Pd, drying/calcining, and reducing with a reducing gas, in particular free hydrogen, at a temperature of about 0-300 °C. Both compositions of matter are used as a catalyst in a process for oxidizing CO to CO₂, e.g., in a CO₂ laser.

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OXIDATION OF CARBON MONOXIDE AND CATALYST THEREFOR

Background of the Invention

5 This invention relates to the oxidation of carbon monoxide to carbon dioxide. In another aspect, this invention relates to the catalytic oxidation of carbon monoxide, in particular under conditions suitable for laser applications. In a further aspect, this invention relates to effective CO oxidation catalyst compositions. In still another aspect, this invention relates to a process for preparing CO oxidation catalyst compositions.

10 The use of catalysts for the oxidation of carbon monoxide to carbon dioxide by reaction with oxygen, in particular at low temperature, is of much interest, e.g., in breathing masks designed to remove CO from inhaled air, and in CO₂ lasers for combining CO and O₂ formed by dissociation of CO₂ during discharge. In the latter application, the presence of O₂ is most undesirable because it can cause a breakdown of the electrical field in the laser cavity. Several patents, such as U.S. Patents 4,490,482 and 4,639,432, disclose compositions useful as CO oxidation catalysts in CO₂ laser applications. However, there is an ever present
15 need to develop new, effective CO oxidation catalyst compositions and/or improved processes for preparing effective CO oxidation catalyst compositions.

Summary of the Invention

20 It is an object of this invention to provide a composition of matter which is effective as a catalyst for the oxidation of carbon monoxide with free oxygen. It is another object to provide a process for preparing a composition of matter which is effective as a catalyst for the oxidation of carbon monoxide. It is a further
25 object of this invention to provide an effective process for catalytically oxidizing carbon monoxide. Other objects and advantages will be apparent from the detailed description and the claims.

In accordance with this invention, a process for preparing a composition of matter comprising Pt and/or Pd metal and TiO₂ (suitable and effective as a catalyst composition for the oxidation of carbon monoxide by reaction with free oxygen) comprises the steps of:

30 (a) contacting (preferably impregnating)
a support material (from which silica is substantially absent) comprising (preferably consisting essentially of) titanium dioxide (titania)
with a solution comprising at least one dissolved compound of at least one noble metal selected from the group consisting of platinum and palladium (preferably Pt);

35 (b) heating the material obtained in step (a) under such conditions as to substantially dry said material obtained in step (a) and to at least partially (preferably substantially) convert said at least one compound of Pt and/or Pd to at least one of oxides of Pt, oxides of Pd, Pt metal and Pd metal; and

(c) heating the material obtained in step (b) in a reducing gas atmosphere, preferably a free hydrogen containing gas, more preferably a stream of H₂, at a temperature in the range of from about 300 to about
40 800 °C, under such conditions as to activate said material obtained in step (b), i.e. to make the material obtained in step (b) more active as a catalyst for CO oxidation by reaction with O₂, and to form (obtain) the composition of matter defined above.

In a preferred embodiment, heating step (b) is carried out in two sub-steps:

45 (b1) heating the material obtained in step (a) at a first temperature so as to remove substantially all liquids [i.e., the solvent of the solution used in step (a)] from said material obtained in step (a), and

(b2) heating (calcining) the substantially dried material obtained in step (b1) at a second temperature, which is higher than said first temperature, so as to at least partially (preferably substantially) convert said at least one compound of Pt and/or Pd to at least one of oxides of Pt, oxides of Pd, metallic Pt and metallic
50 Pd (i.e., Pt oxide and/or Pd oxide and/or Pt metal and/or Pd metal).

In another preferred embodiment, the solution used in step (a) additionally comprises at least one dissolved compound of at least one metal selected from the group consisting of rhenium, iron, ruthenium, copper and silver, which are at least partially (preferably substantially) converted to metal oxides in step (b) or, alternatively, step (b2). In another preferred embodiment, compounds of chromium, manganese and zinc

are substantially absent (besides silica) from the material obtained in step (c). In a further preferred embodiment, the titania support material, before its being used in step (a) has been extracted with an aqueous acidic solution (so as to remove undesirable impurities therefrom), treated with an alkaline solution, washed (e.g., with water), dried, and then calcined (e.g., at about 200-800 °C, preferably for about 0.5-10 hours).

In a particular preferred embodiment, a process for preparing a composition of matter comprising Pt and/or Pd metal and TiO₂ (effective as a CO oxidation catalyst composition) comprises the step of:

(A) impregnating a porous ceramic material (preferably monolith material, i.e., a porous ceramic honeycomb material) with a colloidal dispersion (also referred to as a colloidal solution) of titania in a suitable liquid dispersion medium (preferably water), wherein dispersed silica is substantially absent in said colloidal dispersion;

(B) heating the titania-coated material obtained in step (A) so as to obtain a substantially dried titania-coated monolith material;

(C) contacting (preferably impregnating) the titania-coated ceramic material (preferably monolith material) obtained in step (B) with a solution (preferably aqueous), comprising at least one dissolved compound of at least one noble metal selected from the group consisting of platinum and palladium (preferably Pt);

(D) heating the material obtained in step (C) under such conditions as to substantially dry the material obtained in step (C) and to at least partially (preferably substantially) convert said at least one compound of Pd and/or Pt to at least one of oxides of Pt, oxides of Pd, Pt metal and Pd metal; and

(E) heating the material obtained in step (D) in a reducing gas atmosphere, preferably a free hydrogen containing gas, more preferably a stream of H₂, at a temperature in the range of from about 0 °C to about 300 °C, under such conditions as to activate said material obtained in step (D), i.e., to make it more active as a CO oxidation catalyst, and to form (obtain) the composition defined above.

The impregnation step (A) can be carried out once or twice or more than twice in sequence, so as to ensure adequate coating of the monolith with TiO₂. Step (D) can be carried out as a sequence of sub-steps: drying sub-step (D1) and calcining sub-step (D2). The conditions of drying steps (B) and (D1) are substantially the same as those of drying sub-step (b1), described above. The conditions of calcining sub-step (D2) is substantially the same as those of calcining sub-step (b2), described above.

Also in accordance with this invention, there is provided a composition of matter (useful and effective as a catalyst composition for the oxidation of CO with O₂), from which silica is substantially absent, comprising (i) a support material comprising (preferably consisting essentially of) titania and (ii) at least one noble metal selected from the group consisting of Pt and Pd; said composition of matter having been prepared by the process, described above, comprising steps (a), (b) and (c); or, alternatively, steps (a), (b1), (b2) and (c); or, preferably, steps (A), (B), (C), (D) and (E), as defined above. Preferably said composition of matter comprises Pt and additionally (iii) at least one substance selected from the group consisting of rhenium oxide, iron oxide, ruthenium metal, ruthenium oxide, copper metal, copper oxide, silver metal silver oxide, samarium oxide and europium oxide, preferably iron oxide. In one preferred embodiment, the composition of matter of this invention consists essentially of components (i) and (ii). In another preferred embodiment, the composition of matter consists essentially of component (i), Pt metal and component (iii).

Further in accordance with this invention, a process for oxidizing carbon monoxide comprises contacting a gas comprising CO and O₂ with a catalyst composition (from which silica is substantially absent) comprising titania and at least one noble metal selected from the group consisting of Pt and Pd; said catalyst composition having been prepared by a process comprising steps (a), (b) and (c); or, alternatively, (a), (b1), (b2) and (c); or, preferably, (A), (B), (C), (D) and (E), as defined above, under such conditions as to at least partially (preferably substantially) convert CO and O₂ to CO₂.

Preferably, in the CO oxidation in process of this invention the catalyst composition of this invention (described above) additionally comprises component (iii), as defined above, preferably iron oxide (e.g., FeO and/or Fe₂O₃ and/or Fe₃O₄). Also preferably, compounds of Cr, Mn and Zn are substantially absent from the catalyst composition (besides SiO₂). In a preferred embodiment, the CO oxidation process of this invention is carried out at a temperature of below 400 °C (more preferably from about -30 °C to about 170 °C). In another preferred embodiment, the CO oxidation process is carried out in a CO₂ laser so as to recombine CO and O₂, which have been formed by decomposition of CO₂.

Brief Description of the Drawings

FIGURE 1 shows the CO conversion, during oxidation of CO at low temperature, as a function of the temperature during the reducing pretreatment of a Pt/TiO₂ catalyst with H₂.

FIGURE 2 illustrates the effect of copromoters on the catalytic activity of a Pt/TiO₂ catalyst when used for low temperature oxidation of CO.

FIGURE 3 illustrates the effect of copromoters on the catalytic activity of a Pt/Fe/TiO₂ catalyst when used for low temperature oxidation of CO.

Detailed Description of the Invention

Any titania-containing support material can be used as the support material (i). Titania, as the preferred support material, is commercially available. The method of preparation of titania is not considered critical. Titania can be prepared by flame hydrolysis of volatile titania compounds; or by precipitation from an aqueous solution of titanium compounds with an alkaline reagent, followed by washing, drying and calcining; and the like. If mixtures of titania with alumina and/or magnesia are used, any suitable weight ratio can be used (such as from 1-99 weight-% TiO₂ and from 99-1 weight-% Al₂O₃ and/or MgO).

Generally the surface area (determined by the BET/N₂ method; ASTM D3037) of titania is in the range of from about 10 to about 300 m²/g. Titania can have spherical, trilobal, quadrilobal or irregular shapes. When titania spheres are used, their diameter generally is in the range of from about 0.5 to about 5 mm. Silica should be substantially absent from the support material (i.e., silica should not be present at a level higher than about 0.5, preferably about 0.2, weight-% each).

It is within the scope of this invention to prepare suitable support materials by coating a porous ceramic material, such as a monolith (commercially available from Corning Glass Works, Corning, NY), described in U.S. Patents 4,388,277 and 4,524,051, with titania. Other suitable porous ceramic support materials are glass frits, sintered alumina and the like (such as those disclosed in U.S. Patent 3,963,827). The choice of the ceramic material is determined by cost, pore structure, surface area, attrition resistance and similar factors. The porous ceramic material (preferably a monolith) can be impregnated with organic compounds of Ti (such as a titanium tetraalkoxide), hydrolyzed, dried and calcined. Or the porous ceramic material (preferably monolith) can be impregnated with a dispersion of titania particles, followed by drying and calcining.

In the presently more preferred embodiment of this invention, a monolith is impregnated with a colloidal dispersion (colloidal solution) of titania in step (A). Preferably, colloidal particles of titania having an average particle diameter of about 1 to about 100 nanometers, more preferably about 5 to about 20 nanometers, are dispersed in any suitable liquid dispersion medium, such as water, alcohols, ketones and the like, preferably water. Generally, the concentration of TiO₂ in the colloidal dispersal is in the range of from about 0.1 to about 50, preferably from about 5 to about 25, weight percent TiO₂. The weight ratio of colloidal dispersion of TiO₂ to monolith material in step (A) is chosen so as to provide a TiO₂ content of the material obtained in step (B) in the range of from about 1 to about 40 weight-% TiO₂, preferably about 5 to about 30 weight-% TiO₂.

The impregnation of the titania-containing support material with Pt and/or Pd (preferably Pt) in steps (a) and (c), respectively, can be carried out in any suitable manner. First, compounds of Pt and/or Pd are dissolved in a suitable solvent (preferably water) so as to prepare solutions of suitable concentration, generally containing from about 0.005 to about 0.20, preferably about 0.01 to about 0.1, g Pt and/or Pd per cc of solution. Non-limiting examples of suitable compounds of Pt and Pd are: PtCl₂, PtCl₄, H₂PtCl₆, PtBr₄, Pt(NH₃)₄Cl₂, Pt(NH₃)₄(NO₃)₂ and the like; PdCl₂, PdCl₄, H₂PdCl₆, Pd(NH₃)₄(NO₃)₂ and the like; preferably (at present) Pt(NH₃)₄(NO₃)₂ and Pd(NH₃)₄(NO₃)₂. The TiO₂-containing support material is then impregnated by soaking it in the solution of Pt and/or Pd compounds; or (less preferably) the Pt and/or Pd containing solution is sprayed onto the support material. The ratio of Pt and/or Pd containing solution to support material generally is such that the final catalyst obtained in step (c) or, alternatively, the coating of the material obtained in (E), i.e., the material obtained in step (E) excluding the monolith, contains about 0.5 to about 5, preferably about 1 to about 3, weight-% Pt or Pd. When a solution containing both Pt and Pd compounds, the level of Pt and Pd generally is about 0.5 to about 5, preferably about 1 to about 3, weight percent (Pt + Pd).

In a preferred embodiment, at least one compound of a metal selected from the group of Re, Fe, Ru,

Cu, Ag, Sm and Eu, more preferably Fe, is also present as a copromoter in the impregnating solution besides at least one Pt compound. Non-limiting examples of suitable Fe compounds that can be used as solutes are FeCl_2 , FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, $\text{Fe}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and the like, preferably compounds of Fe in the valence state +3, more preferably $\text{Fe}(\text{NO}_3)_3$. Non-limiting examples of Mn compounds are MnCl_2 , MnSO_4 , $\text{Mn}(\text{NO}_3)_2$, KMnO_4 , and the like. Non-limiting examples of Ru compounds are RuCl_3 , RuF_4 , $\text{Ru}(\text{NH}_3)_5\text{Cl}_3$, KRuO_4 , and the like. Non-limiting examples of Cu compounds are CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, CuSO_4 , $\text{Cu}(\text{II})$ acetate, ammine complexes of the above Cu salts, and the like. Non-limiting examples of Ag compounds are AgF , AgNO_3 , Ag_2SO_4 , Ag acetate, ammine complexes of the above Ag salts, and the like. Non-limiting examples of Sm compounds are SmCl_3 , $\text{Sm}(\text{NO}_3)_3$, $\text{Sm}_2(\text{SO}_4)_3$, and the like. Non-limiting examples of EuCl_3 , $\text{Eu}(\text{NO}_3)_3$, $\text{Eu}_2(\text{SO}_4)_3$ and the like.

Generally, the concentration of the copromoter compound (expressed as metal) is in the range of from about 0.01 to about 0.4, preferably about 0.02 to about 0.2, g metal (i.e., Mn or Fe or Ru or Cu or Ag or mixtures thereof) per cc solution. When a mixture of copromoter compounds is used, e.g., a mixture of compounds of Fe and Ru, Fe and Ag, Ru, Cu, Sm and Eu, Fe/Ru/Ag, and the like, the total concentration of copromoter metals is about 0.02-0.8 g/cc. The impregnation of the support material with Pt and/or Pd and the copromoter can be carried out either by sequential impregnation (first Pt or Pt + Pd, then copromoter; or vice versa), or by simultaneous impregnation in step (a) or step (C) (i.e., using a solution containing compounds of Pt or Pt + Pd and of at least one copromoter compound).

When sequential impregnation is employed, the impregnation with a solution of at least one copromoter compound is carried out after heating step (b) and before step (c); or, if applicable, after heating step (D) and before step (E). Thus, an impregnating step (a*) with at least one dissolved copromoter compound and heating step (b*) [carried out in substantially the same manner as step (b)] are performed after step (b) and before step (c). Similarly, an impregnation step (C*) with at least one dissolved copromoter compound and heating step (D*) [carried out in substantially the same manner as step (D)] are performed after step (D) and before step (E). The ratio of copromoter containing solution to support material is such as to provide a level of about 0.2 to about 4, preferably about 0.5-2, weight percent copromoter metal (i.e., Re or Fe or Ru or Cu Ag, Sm or Eu, or mixtures of two or more metals, (e.g., Fe/Ag, and the like) on the material obtained in step (c) or, alternatively, on the material obtained in step (E), excluding the porous ceramic material (preferably monolith).

Preferably compounds of Cr, Mn and Zn should be substantially absent from the impregnating solutions used in impregnation steps (a), (a*), (C) and (C*) since these compounds have a detrimental effect on the activity for CO oxidation of the finished catalyst.

Heating step (b) is generally carried out in an inert or oxidizing atmosphere, preferably a free oxygen containing gas atmosphere (such as air), generally at a temperature ranging from about 30 to about 700 °C. Preferably, heating step (b) is carried out in two sequential sub-steps: sub-step (b1), at about 30 to about 200 °C (preferably at 80-130 °C), generally for about 0.5 to about 10 hours, so as to substantially dry the impregnated material obtained in step (a) (preferably under such conditions as to reduce the level of adhered and occluded water to less than about 20 weight-%); and sub-step (b2), at about 300 to about 700 °C (preferably about 400 to about 600 °C), generally for about 1 to about 20 hours, under such conditions as to substantially calcine the impregnated support material so as to obtain oxides of Pt and/or Pd, on titania. When compounds of Re, Fe, Ru, Cu, Ag, Sm, Eu or mixtures thereof have been present in the Pt and/or Pd-containing impregnating solution, generally oxides of Re, Fe, Ru, Cu, Ag, Sm, Eu or mixtures are formed in step (b2).

Drying sub-steps (b*1), (D1) and (D*1), described above, are carried out at conditions which are essentially the same as those described for sub-step (b1). And calcining sub-steps (b*2), (D2) and (D*2), described above, are carried out at conditions which are essentially the same as those described for sub-step (b2).

Reducing step (c) can be carried out in any suitable manner at a temperature in the range of from about 300 to about 800 °C, preferably from about 350 to about 500 °C. Reducing step (E) can be carried out in any suitable manner at a temperature in the range of from about 0 to about 300 °C, preferably about 20 to about 200 °C. Any reducing gas can be employed in reducing steps (c) and (E), such as a gas comprising H_2 , CO, gaseous hydrocarbons such as methane, mixtures of the above, and the like. Preferably, a free hydrogen containing gas, more preferably substantially pure H_2 , is employed. Reducing steps (c) and (E) can be carried out for any suitable period of time suitable to activate the calcined material obtained in the previous step, preferably from about 0.5 to about 20 hours. Pt and/or Pd exist substantially as Pt and/or Pd metal after reducing steps (c) and (E), respectively. However, small amounts of oxides of Pt and/or Pd may also be present.

The process for oxidizing a carbon monoxide containing feed gas can be carried at any suitable

temperature and pressure conditions, for any suitable length of time, at any suitable gas hourly space velocity, and any suitable volume ratio of CO and O₂. The reaction temperature generally is in the range of from about -50 to about 400 °C, preferably from about -30 to about 170 °C, more preferably from about 10 to about 50 °C. The pressure during the oxidation process generally is in the range of from about 1 to about 2,000 psia, more preferably from about 5 to about 20 psia. The volume ratio of CO to O₂ in the feed gas can range from about 1:100 to about 100:1, and preferably is in the range of about 1:10 to about 10:1. The volume percentage of CO and the volume percentage of O₂ in the feed gas can each be in the range of from about 0.05 to about 50, preferably from about 0.5 to about 3. The gas hourly space velocity (cc feed gas per cc catalyst per hour) can be in the range of from about 0.5 to about 10,000, preferably from about 1 to about 1,000. It is understood that the calculation of the gas hourly space velocity is based on the volume of the active catalyst i.e., the titania-supported Pt and/or Pd catalyst (optionally also containing copromoter), excluding the volume occupied by any additional support material, such as a monolith material.

The feed gas can be formed in any suitable manner, e.g., by mixing CO, O₂ and optionally other gases such as CO₂, N₂, He and the like, such as in a carbon dioxide laser cavity. Or the feed gas can be an exhaust gas from a combustion engine, or it can be air that is to be inhaled by humans and contains undesirable levels of toxic carbon monoxide, and the like. The feed gas can be contacted in any suitable vessel or apparatus, such as in a laser cavity or in an exhaust pipe of a combustion engine, or in a gas mask used by humans, wherein the feed gas passes over the catalyst composition of this invention at the conditions described above. The CO oxidation process of this invention can be carried out in any suitable setting and for any purpose, e.g., for recombining CO and O₂ in CO₂ lasers, to oxidize CO contained in exhaust gases or air, to make isotopically labeled CO₂ from CO and the ¹⁸O isotope, and the like.

The following examples are presented in further illustration of the invention and are not to be construed as unduly limiting the scope of the invention.

Example I

This example illustrates the experimental setup for testing the activity of noble metal catalysts for catalyzing the oxidation of carbon monoxide (so as to simulate catalytic recombination of CO and O₂ in CO₂ lasers). A gaseous feed blend comprising CO, O₂, He and N₂ was passed through a needle valve and a glass reactor in an upflow direction. The glass reactor tube had an inner diameter of about 6 mm and generally contained about 1.0 gram catalyst in a bed of about 2.5 cm height. The temperature in the catalyst bed was measured by means of a thermocouple inserted into the top layer of the catalyst bed. The CO content in the reactor effluent was determined by means of a Beckman Model 864 IR analyzer.

All tests were carried out at ambient conditions. Generally the temperature in the catalyst bed rose to about 30 °C because of the generation of heat during the CO oxidation tests. The feed rate of the gaseous feed stream generally was in the range of about 4-300 cc/minute.

Example II

This example illustrates the preparation of titania-supported catalyst compositions and their performance in CO oxidation tests.

catalyst A1 contained 1 weight-% Pt on TiO₂. It was prepared by mixing, at room temperature, 30 g of flame-hydrolyzed titania (provided by Degussa Corporation, Teterboro, NJ; having a BET/N₂ surface area of about 50 m²/g) with 31 cc of aqueous chloroplatinic acid solution, which contained 0.0096 g Pt/cc solution, and enough distilled water to form a thick paste. After impregnation, Catalyst A1 was dried at about 125 °C for several hours and calcined in air at about 350 °C for about 6 hours. Catalyst A1 was then pretreated with hydrogen gas for about 4 hours at various temperatures (range: 200-725 °C).

Samples of catalyst A1 (1% Pt/TiO₂) that had been pretreated with H₂ at different temperatures was tested at room temperature (about 27 °C) in the CO oxidation unit described in Example I. The gaseous feed blend contained 1.2 volume-% CO, 0.6 volume-% O₂, 40.7 volume-% N₂ and 57.5 volume-% He. The feed rate was 10 cc/minute. The correlation between CO conversion and the temperature of the hydrogen pretreatment temperature of Catalyst A1 is shown in Figure 1. Figure 1 shows that H₂ pretreatment of the Pt/TiO₂ catalyst at temperatures in the range of 400 to 725 °C resulted in a considerably more active CO oxidation catalyst than H₂ pretreatment at 200 °C.

Catalyst A2 contained 1 weight-% Pt and 0.3 weight-% Pd on TiO₂, and was prepared by mixing 30 g Catalyst A1 with 100 cc of an aqueous solution containing 0.25 g tetramminepalladium(II) nitrate, drying and calcining the obtained paste as described for Catalyst A1. The calcined Catalyst A2 material was then activated by heating with H₂ at 725 °C for 16 hours. CO conversion (measured as described for the tests employing Catalyst A1) was 100% for about 126 hours. Thus, Pd enhanced the CO oxidation activity of the Pt/TiO₂ catalyst.

Example III

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This example illustrates the effects of various other copromoters on the CO oxidation activity of a Pt/TiO₂ catalyst which contained 2 weight-% Pt (labeled Catalyst B1) and was prepared substantially in accordance with the procedure for Catalyst A1, except that the Pt concentration in the impregnating solution was thrice as high, and the TiO₂ support material was provided by Calsicat (division of Mallinckrodt, Inc., St. Louis, MO) and had a BET surface area of about 40-170 m²/g.

Catalyst B1 was then mixed with aqueous solutions containing different metal compounds so as to provide a copromoter level of 0.8 weight-% of the metal. A solution of tetramminepalladium(II) nitrate was used to make Catalyst B2 (0.8% Pd/2% Pt/TiO₂). A solution of RuCl₃•3H₂O was used to make Catalyst B3 (0.8% Ru/2% Pt/TiO₂). A solution of ReCl₃ was used to make Catalyst B4 (0.8% Re/2% Pt/TiO₂). A solution of hexamminechloroiridium(II) dichloride was used to make Catalyst B5 (0.8% Ir/2% Pt/TiO₂). A solution of Cu(NO₃)₂•2.5H₂O was used to make Catalyst B6 (0.8% Cu/2% Pt/TiO₂). A solution of Fe(NO₃)₃•9H₂O was used to make Catalyst B7 (0.8% Fe/2% Pt/TiO₂).

CO conversions attained at room temperature (about 27 °C) in the test unit of Example I employing a gas feed containing 1.2 volume-% CO, 0.6 volume-% O₂, 48 volume-% N₂ and He as the balance (flow rate of feed: 10 cc/minute), are shown for Catalysts B1, B2, B3, B4, B5, B6 and B7 in Figure 2. All catalysts had been pretreated with hydrogen gas for 3 hours at 600 °C.

The graphs in Figure 2 indicate that Fe, Pd, Re, Ru and Cu consistently enhanced the CO oxidation activity of the Pt/TiO₂ base catalyst, whereas Ir enhanced the CO oxidation activity of the base catalyst only up to 60 hours on stream. Additional test data (not shown in Figure 2) indicated that Rh did not affect the catalytic activity of the Pt/TiO₂ base catalyst. Fe, Pd and Re were the most effective copromoters for the Pt/TiO₂-containing CO oxidation catalyst.

In another test series, a TiO₂-supported catalyst containing 0.4 weight-% Fe and 2.0 weight-% Pt, labeled Catalyst B8, was prepared substantially in accordance with the procedure for Catalyst B7, except for a lower Fe level. Catalyst B8 was then impregnated with an aqueous solution containing a compound of a third promoter metal, so as to obtain Catalysts B9, B10, B11 and B12, respectively, containing 0.1 weight-% of the following third promoter elements: Mn, Cr, Ag and Zn. Carbon monoxide conversions, attained by Catalysts B8, B9, B10 and B11 at room temperature (about 27 °C) in the test unit of Example I employing the gas feed described in Example II are shown in Figure 3. The gas feed rate was 60 cc/minute (in lieu of 10 cc/minute). All catalysts had been pretreated in hydrogen gas for 3 hours at about 500 °C. The TiO₂ support had been heated in H₂ for about 48 hours at 500 °C before impregnation with the promoters (Fe, Pt + third promoter) for removal of traces of sulfur in TiO₂.

The graphs in Figure 3 indicate that Ag enhanced the activity of the Fe/Pt/TiO₂ CO oxidation catalyst, whereas the presence of Mn, Cr and Zn was detrimental. Based on these test results, it is concluded that Ag is also an effective promoter for a Pt/TiO₂-containing catalyst (with or without Fe).

Example IV

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This example illustrates a preferred feature of the preparation of TiO₂-supported Pt catalysts useful for CO oxidation at low temperature. Two catalysts containing 0.5 weight-% Fe, and 2.0 weight-% Pt on Calsicat TiO₂ support were tested. Catalyst C1 was prepared substantially in accordance with the preparation of Catalysts B7 and B8, using an aqueous solution of chloroplatinic acid. Catalyst C2 was prepared as described above except that the dissolved Pt compound was tetrammineplatinum(II) nitrate. The two catalysts were dried, calcined and pretreated with hydrogen gas at 500 °C for about 3 hours, as has been described in Examples II and III. X-ray diffraction test results indicated that Pt existed in Catalyst

C substantially as metallic Pt.

The two catalysts were tested at room temperature (about 26 ° C) in the CO oxidation test unit described in Example I, employing the gas feed described in Example III. The gas feed rate was 120 cc/minute. Test results are summarized in Table I.

Table I

Catalyst	Hours on Stream	% CO Converted	cc/Minute CO Converted
C1	2	60	0.84
	6	56	0.78
	10	56	0.78
	14	55	0.77
	20	55	0.77
	30 ¹	50	0.70
	40 ¹	44	0.62
C2	2	63	0.89
	6	70	0.98
	10	78	1.09
	20	89	1.25
	30	94	1.32
	40	92	1.30
	50	92	1.30
	60	90	1.26
	70	91	1.27

¹Temperature had dropped to 23 ° C.

Test results in Table I clearly show that the Fe/Pt/TiO₂ catalyst prepared using a chloride-free Pt compound for impregnation (Catalyst C2) was consistently more active for CO oxidation than Catalyst C1, which had been prepared using a chloride-containing Pt compound for impregnation.

Example V

This example illustrates how the CO oxidation activity of a TiO₂-supported catalyst can be enhanced by pretreatment of the TiO₂ support.

25 grams of flame-hydrolyzed titania (provided by Degussa Corporation; see Example II) was stirred overnight in a mixture of 200 cc concentrated H₂SO₄ and 300 cc deionized water. The aqueous slurry of titania was then neutralized with a concentrated ammonia solution. The dispersed titania was allowed to settle, and the supernatant solution was decanted. The thus treated titania was washed four times with deionized water and dried in a circulating air oven (80-90 ° C; 5 hours).

5 grams of the acid-treated TiO₂ was impregnated with 3 cc of an aqueous solution of Pt(NH₃)₄(NO₃)₂ - (containing 0.033 g Pt per cc) and then with 2.5 cc of an aqueous solution of Fe(NO₃)₃ (containing 0.01 g Fe per cc). The thus impregnated material was dried, calcined and pretreated with hydrogen gas for 3 hours at 500 ° C. This catalyst, labeled Catalyst D, contained 2 weight-% Pt and 0.5 weight-% Fe.

Catalyst D was compared to Catalyst C2 (see Example IV; also containing 2 weight-% Fe on TiO₂) which had been prepared without acid treatment of titania (provided by Degussa Corporation). The two catalysts were tested at room temperature (27-29 ° C) in the CO oxidation test unit described in Example I, employing the gas feed described in Example III. Test results are summarized in Table II.

Table II

Catalyst	Gas Feed Rate (cc/min.)	Hours on Stream	% CO Converted	cc/Minute CO Converted
D (TiO ₂ Support Acid-Treated)	160	2	58	1.09
	"	4	65	1.22
	"	6	68	1.28
	"	10	68	1.28
	"	14	68	1.28
	"	18	67.5	1.26
	"	22	67.5	1.26
C2 (TiO ₂ Support Not Acid-Treated)	120	2	56	0.79
	"	4	48	0.67
	"	6	43	0.60
	"	10	41	0.58
	"	14	41	0.58
	"	18	42	0.59

Data in Table II clearly indicate that the CO conversion was greater for Catalyst D as compared to Catalyst C2 in spite of the higher gas feed rate of the run with Catalyst D. The conversion of CO, expressed in cc CO converted per minute, attained by Catalyst D was about twice that attained by Catalyst C2.

Thus, in the presently preferred catalyst preparation method of this invention, the TiO₂ support material is treated with an aqueous acid solution, followed by neutralization and washing, before the TiO₂ support material is impregnated with promoters, dried, calcined and heated in H₂ gas.

Example VI

This example illustrates the use of honeycomb ceramic catalyst supports, called monoliths, for preparing Pt/TiO₂-containing catalysts employed in the oxidation of carbon monoxide. The two best modes of preparation of these honeycomb catalysts are described in this example.

Mode A:

A round piece of Celcor® Cordierite #9475 monolith ceramic material 2MgO•2Al₂O₃•5SiO₂; provided by Corning Glass Works, Corning, NY; diameter: 1 inch; height: 1 inch; having 100 cells per square inch) was dried for 2 hours at 185° C, and was then dipped about 7 times into a stirred suspension of 30 grams flame-hydrolyzed TiO₂ (Degussa Corporation) in 250 cc distilled water. The material was dried after each dipping. This TiO₂-coated monolith material was calcined in air for 4 hours at 500° C. The calcined TiO₂-coated monolith material was then dipped into an aqueous solution of chloroplatinic acid (containing 0.022 g Pt/cc), dried for 1 hour at 300° C, dipped into an aqueous solution of Fe(NO₃)₃ (containing 0.01 g Fe/cc) and dried again for 1 hour at 300° C. The Fe/Pt/TiO₂/monolith catalyst, labeled Catalyst E1, was pretreated in hydrogen gas for 3 hours at 500° C and then heated in helium gas at that temperature for 30 minutes. The impregnation with Pt and Fe, drying and pretreating with H₂ was repeated.

Catalyst E1 was tested in a CO oxidation apparatus at room temperature (about 26° C) in an apparatus similar to the one described in Example I, except that a glass reactor tube of 1 inch inner diameter was used. The feed gas employed was essentially the same as the one described in Example III. Test results are summarized in Table III.

Table III

Hours on Stream	Gas Feed Rate (cc/min.)	% CO Conversion	cc/Minute CO Converted
4	10	99	0.12
10	10	99	0.12
18	10	99	0.12
20	30	96	0.34
24	30	96	0.34
30	60	91	0.64
40	60	80	0.56
50	60	72	0.50
60	60	66	0.46
70	60	58	0.41
80	60	60	0.42
90	60	58	0.41
100	60	56	0.40
110	60	55	0.38

Mode B:

The presently best mode for preparing honeycomb-type Pt/TiO₂-containing catalysts is as follows. A piece of Cordierite 9475 monolith material (diameter: 1 inch; height: 1 inch) was dipped into a colloided solution of TiO₂ in water (provided by Nalco; containing about 6 weight-% TiO₂ having an average particle diameter of 2 microns). The monolith piece was dipped 9 times into the colloidal TiO₂ solution. The thus impregnated piece was dried at 150° C after each dipping. The TiO₂-coated monolith was then dipped into an aqueous (Pt(NH₃)₄(NO₃)₂ solution (containing 0.33 g/cc Pt), dried, calcined in air for 2 hours at 300° C, and pretreated in H₂ gas after 1 hour at room temperature (25° C). The coating of the thus-prepared catalyst, labeled Catalyst E2, contained about 3 weight-% Pt and about 97 weight-% TiO₂.

Catalyst E3 was prepared by dipping E2 into an aqueous solution of Fe(NO₃)₃ (containing 0.01 g Fe per cc), drying, calcining in air for 2 hours at 300° C, and pretreating in H₂ for 1 hour at room temperature. The coating of Catalyst E2 contained about 3 weight-% Pt, about 1 weight-% Fe and 96 weight-% TiO₂.

Catalyst E4 was prepared by dipping E3 into an aqueous solution of Pd(NH₃)₄(NO₃)₂ (containing 0.04 g Pd per cc), calcining in air for 2 hours at 300° C, and pretreating with H₂ for 1 hour at room temperature.

Catalysts E2, E3 and E4 were tested in the experimental setup described for the CO oxidation run employing Catalyst E1. The gas feed rate for all runs was 300 cc/minute. Test results are summarized in Table IV.

Table IV

Catalyst	Hours on Stream	% CO Conversion	cc/Minute CO Converted
E2	1	9.4	0.33
	2	8.5	0.30
	4	4.3	0.15
E3	1	74	2.61
	2	69	2.43
	4	60	2.10
	6	58	2.04
	10	54	1.89
	14	51	1.80
	20	47	1.65
E4	1	93	3.27
	2	83	2.91
	4	73	2.55
	6	69	2.43
	10	55	1.92
	14	47	1.65
	20	33	1.17

Test results in Table IV indicate that high CO conversions (cc CO/minute) were attained at high gas feed rates (300 cc/minute; higher than in any previous run). Thus the monolith-supported catalysts E2-E4, prepared by impregnation with colloidal TiO_2 , are considered the presently best TiO_2 -supported CO oxidation catalysts.

A run not listed in Table IV employing a catalyst similar to Catalyst E3, except that 0.6 weight-% Mn was prepared in the coating in lieu of 1 weight-% Fe, gave CO conversions of only about 33% and about 1.2 cc CO/minute during the first 5 hours. Thus, Mn/Pt/ TiO_2 catalysts are not considered more preferred catalysts of this invention.

A particular advantage of the monolith-supported Pt/ TiO_2 -containing catalysts E2-E4 is that they could be activated by pretreatment in H_2 at a low temperature (about 25°C), whereas the catalysts used in previous examples required pretreatment in H_2 at an elevated temperature (e.g., 400 - 500°C). In fact, reheating Catalyst E4 for 3 hours in air at 500°C and then for 1 hour in hydrogen at 400°C made this catalyst substantially inactive for CO oxidation.

Example VII

A test employing a catalyst, which contained 1 weight-% Pt on SiO_2 and had been prepared in H_2 at 660°C for about 1 hour, showed no activity for catalyzing the oxidation of CO at room temperature. Thus, SiO_2 should be substantially absent from the catalyst of this invention.

Example VIII

This example illustrates the effect of two lanthanides on the performance of a Pt/ TiO_2 catalyst.

Catalyst F1 (2.0 weight-% Pt on TiO_2) was prepared by impregnating 3/16" pellets of Calsicat titania (see Example II) with a first portion of an aqueous solution of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ comprising 0.02 g Pt/cc solution, followed by drying at 125°C , impregnating with the second portion of the impregnating solution, again followed by drying at 125°C , and finally calcined in air at 300°C for 3 hours.

Two gram samples of Catalyst F1 were now impregnated with 1 cc of an aqueous lanthanide promoter solutions. Catalyst F2 (0.7 weight-% Sm and 2.0 weight-% Pt on TiO_2) was prepared by impregnating F1 with 1 cc of an aqueous solution of $\text{Sm}(\text{NO}_3)_3$ containing 0.14 g Sm, and drying. Catalyst F3 (0.7 weight-%

Eu and 2.0 weight-% Pt on TiO₂) was prepared by impregnating F1 with an aqueous solution of Eu(NO₃)₃ containing 0.14 g Eu, and drying.

Catalyst F1, F2, and F3 were calcined in air at 400 °C for two hours and then heated in hydrogen gas at 200 °C for 1.5 hours. The activity of Catalyst F1 through F4 was determined in the CO oxidation test apparatus described in Example I. The feed gas contained in 1.25 volume-% CO, 0.6 volume-% O₂, 32 volume-% CO₂, 32 volume-% He, and N₂ as the balance. Test results are summarized in Table V.

Table V

Catalyst	Hours on Stream	Temp. (°C)	Feed Rate (cc/minute)	% CO Conversion	CC/Minute CO Converted*
F1 (Pt/TiO ₂)	1	24	20	16	0.04
	2	50	20	29	0.07
	3	100	30	94	0.35
	4	100	30	93	0.35
	6	100	30	91	0.34
	8	100	30	91	0.34
	10	100	30	91	0.34
	12	100	30	92	0.35
	14	100	30	92	0.35
	16	100	30	93	0.35
	18	100	30	93	0.35
F2 (Sm/Pt/TiO ₂)	1	24	30	16	0.06
	2	50	30	27	0.10
	3	100	87	67	0.75
	4	100	87	72	0.78
	6	100	87	72	0.78
	8	100	87	72	0.78
	10	100	87	72	0.78
	12	100	87	72	0.78
	14	100	87	72	0.78
	16	100	87	72	0.78
	18	100	87	72	0.78
F3 (Eu/Pt/TiO ₂)	1	24	20	18	0.04
	2	50	20	25	0.06
	3	100	65	79	0.64
	4	100	65	77	0.62
	6	100	65	75	0.61
	8	100	65	73	0.59
	10	100	65	71	0.58
	12	100	65	70	0.57
	14	100	65	68	0.55
	16	100	65	68	0.55
	18	100	65	68	0.55

* per gram catalyst

Based on the test results in Table V, it is concluded that Sm and Eu (as oxides) were effective as copromoters for a Pt/TiO₂ CO oxidation catalyst. Sm/Pt/TiO₂ was more active than Eu/Pt/TiO₂, under the testing conditions of this example.

Example IX

This example illustrates the performance of several Pd/TiO₂ CO oxidation catalysts.

5 Catalyst G1 (2.0 weight-% Pd on TiO₂) was prepared in accordance with the procedure for Catalyst F1 except that an aqueous solution of Pd(NH₃)₄(NO₃)₂ comprising 0.02 g Pd/cc solution was used in lieu of the Pt(NH₃)₄(NO₃)₂ solution.

Catalyst G2 (0.7 weight-% Cr and 2.0 weight-% Pd on TiO₂) was prepared by impregnating 2 grams of G1 with 2 cc of an aqueous solution chromium salt solution containing 0.007 g Cr per cc solution. Catalyst
10 G3 (0.7 weight-% Mn and 2.0 weight-% Pd on TiO₂) was prepared by impregnating 2 grams of G1 with 1.4 cc of an aqueous manganese salt solution containing 0.01 g Mn per cc solution. Catalyst G4 (0.7 weight-% Ni and 2.0 weight-% Pd on TiO₂) was prepared by impregnating 2 grams of G1 with 2.0 cc of an aqueous nickel salt solution containing 0.007 g Ni per cc solution. Catalyst G5 (0.7 weight-% Fe and 2.0 weight-% Pd on TiO₂) was prepared by impregnating 2.0 grams of G1 with 1.2 cc of an aqueous iron salt solution
15 containing 0.012 g Fe per cc solution. Catalyst G6 (0.7 weight-% Ag and 2.0 weight-% Pd on TiO₂) was prepared by impregnating 2 grams of G1 with 2 cc of an aqueous silver salt solution containing 0.007 g Ag per cc solution.

 The above-described preparation of G2 through G6 was carried out by impregnating 2 grams of G1 with 1/2 of the metal salt solution, followed by drying at 125° C for 1 hour, impregnating with the second half of
20 the metal salt solution, and again followed by drying at 125° C for 1 hour. Catalysts G1-G6 were calcined in air at 400° C for 1 hour, and then heated in hydrogen gas at 200° C for 2 hours, before the catalysts were used in CO oxidation tests (as discussed in Example VIII). Test results are summarized in Table VI.

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Table VI

Catalyst	Hours on Stream	Temp. (°C)	Feed Rate (cc/minute)	% CO Conversion	CC/Minute CO Converted*
G1 (Pd/TiO ₂)	1	24	50	21	0.13
	2	50	70	79	0.69
	3	50	70	75	0.66
	4	50	70	73	0.64
	6	50	70	69	0.60
	8	50	70	66	0.58
	10	50	70	65	0.57
	12	50	70	64	0.56
	14	50	70	64	0.56
	16	50	70	64	0.56
	18	100	160	97	1.94
	20	100	160	96	1.92
	22	100	160	94	1.89
	24	100	160	93	1.86
G2 (Cr/Pd/TiO ₂)	1	24	40	16	0.08
	2	50	40	38	0.19
	3	50	40	32	0.16
	4	50	40	28	0.14
	6	50	40	26	0.13
	8	50	40	26	0.13
	10	50	40	26	0.13
	12	50	40	26	0.13
	14	50	40	26	0.13
	16	50	40	26	0.13
	18	100	73	59	0.54
	20	100	73	59	0.54
	22	100	73	59	0.54
G3 (Mn/Pd/TiO ₂)	1	24	40	49	0.24
	2	50	60	74	0.56
	3	50	60	71	0.53
	4	60	60	68	0.51
	6	50	60	63	0.47
	8	50	60	60	0.45
	10	50	60	57	0.43
	12	50	60	54	0.40
	14	50	60	51	0.38
	16	50	60	51	0.38
	18	100	80	95	0.95
	20	100	80	95	0.95

*per gram catalyst

Table VI (Continued)

Catalyst	Hours on Stream	Temp. (°C)	Feed Rate (cc/minute)	% CO Conversion	CC/Minute CO Converted*
G4 (Ni/Pd/TiO ₂)	1	24	20	16	0.04
	2	50	40	49	0.24
	3	50	40	43	0.22
	4	50	40	40	0.20
	6	50	40	36	0.18
	8	50	40	34	0.17
	10	50	40	33	0.16
	12	50	40	32	0.16
	14	50	40	31	0.16
	16	50	40	30	0.15
	18	100	100	82	1.03
	20	100	100	79	0.99
G5 (Fe/Pd/TiO ₂)	22	100	100	78	0.98
	24	100	100	78	0.97
	1	24	100	24	0.24
	2	50	100	61	0.61
	3	50	100	55	0.55
	4	50	100	50	0.50
	6	50	100	44	0.44
	8	50	100	40	0.40
	10	50	100	38	0.38
	12	50	100	36	0.36
	14	50	100	34	0.34
	16	50	100	32	0.32
G6 (Ag/Pd/TiO ₂)	18	100	160	75	1.50
	20	100	160	73	1.46
	22	100	160	71	1.42
	24	100	160	70	1.41
	1	24	20	6	0.01
	2	50	20	52	0.13
	3	50	20	42	0.10
	4	50	20	30	0.08
	6	50	20	26	0.06
	8	50	20	24	0.06
	10	50	20	24	0.06
	12	50	20	24	0.06
	14	50	20	24	0.06
	16	50	20	24	0.06
	18	100	160	71	1.42
	20	100	160	66	1.33
	22	100	160	64	1.28
	24	100	160	64	1.28

*per gram catalyst

Test results summarized in Table VI show that Pd/TiO₂ was a very active CO oxidation catalyst and possessed a catalytic activity comparable to that of a Pt/TiO₂ catalyst (see Catalyst F1, Table V). Test data in Table VI also showed that, under the testing conditions of this example, none of the five copromoters (Cr, Mn, Ni, Fe and Ag) enhanced the catalytic activity of the Pd/TiO₂ base catalyst. The fact that Fe and Ag did not enhance the activity of Pd/TiO₂ is surprising because Fe and Ag were beneficial copromoters for Pt/TiO₂ (see Figures 2 and 3).

Example X

This example illustrates the temperature dependence of the rate of the CO oxidation in the presence of a Fe/Pt/TiO₂ catalyst (Catalyst H: containing 0.7 weight-% Fe and 2.4 weight-% Pt on TiO₂). Catalyst H was prepared as follows.

1.94 grams of Fe(NO₃)₃•9H₂O were dissolved in 48 grams of an aqueous Pt(NH₃)₄(NO₃)₂ solution (containing 0.02 g Pt per cc solution). The above Fe/Pt nitrate solution was diluted with distilled water to a total volume of 60 cc. 30 cc of this diluted solution was mixed in multiple wetting steps with 40 grams of titania, with a drying step (20 minutes at 110° C) after each wetting step. The dried impregnated material was calcined for 2 hours in air at 400° C and then for 2 hours in H₂ at 400° C. Thereafter, the thus-heated Fe/Pt impregnated titania was mixed with the second 30 cc of the above-described diluted Fe/Pt nitrate solution in multiple wetting steps, with a drying step (20 minutes at 110° C) after each wetting step. The thus dried, twice-impregnated material was calcined for 2 hours in air at 400° C and then for hours in hydrogen gas at 200° C.

2 grams of Catalyst H were used in CO oxidation tests, in accordance with the procedure described in Example VIII. Test results are summarized in Tables VII and VIII.

Table VII

Average Reaction* Temp. (° C)	Feed Rate (cc/minute)	CC/Minute CO per g Catalyst Converted
29	463	1.5
42	463	1.7
51	463	1.9
65	930	2.5
76	930	2.8
86	930	3.1
108	930	3.6
128	930	4.1
126	1417	4.2
148	1417	4.7
169	1417	6.1
228	505	2.0

*average of feed inlet temperature and product outlet temperature.

Table VIII

Hours on Stream	Average Reaction Temp. (°C)	Feed Rate (cc/minute)	% CO Conversion	CC/Minute CO Converted*
1	0	300	56	1.05
2	0	300	56	1.05
3	0	300	56	1.05
4	0	300	56	1.05
5	-30	280	46	0.81
6	-30	280	46	0.80
8	-30	280	45	0.78
10	-30	280	45	0.78
15	-30	280	45	0.78
20	-30	280	45	0.78
25	-30	280	46	0.80
30	-30	280	41	0.71

*per gram catalyst, which was treated in H₂ at room temperature for one hour before testing.

Test results in Tables VII and VIII show that the Fe/Pt/TiO₂ CO oxidation catalyst was quite active at elevated temperatures (up to about 170 °C) as well as at a low temperature (as low as -30 °C).

Reasonable variations, modifications and adaptations for various usages and conditions can be made within the scope of the disclosure and the appended claims, without departing from the scope of this invention.

Claims

1. A process for preparing a composition of matter, from which silica is substantially absent, which is useful and effective as a catalyst composition for CO oxidation, and which comprises titania and at least one noble metal selected from the group consisting of platinum and palladium, comprising the steps of:

(a) contacting a support material, from which silica is substantially absent, comprising titania with a solution comprising at least one dissolved compound of at least one noble metal selected from the group consisting of platinum and palladium;

(b) heating the material obtained in step (a) under such conditions as to substantially dry said material obtained in step (a) and to at least partially convert said at least one compound of at least one noble metal to at least one of oxides of Pt, oxides of Pd, Pt metal and Pd metal; and

(c) heating the material obtained in step (b) in a reducing gas atmosphere at a room temperature in the range of from about 300 to about 800 °C, under such conditions as to activate said material obtained in step (b) and to form said composition of matter.

2. A process in accordance with claim 1, wherein said reducing gas atmosphere is a free hydrogen containing gas.

3. A process in accordance with claims 1 or 2, wherein step (b) is carried out in two sub-steps;

(b1) heating the metal obtained in step (a) at a first temperature so as to remove substantially all liquids from said material obtained in step (a), and

(b2) heating the substantially dried material obtained in step (b1) at a second temperature, which is higher than said first temperature, so as to at least partially convert said at least one compound of at least one noble metal to at least one of oxides of Pt; oxides of Pd, metallic Pt and metallic Pd.

4. A process in accordance with claim 3, wherein said first temperature is in the range of from about 30 to about 200 °C, and said second temperature is in the range of from about 300 to about 700 °C.

5. A process in accordance with any of the preceding claims wherein said composition of matter comprises Pt as noble metal and additionally at least one copromoter selected from the group consisting of rhenium oxide, iron oxide, ruthenium metal, ruthenium oxide, copper metal, copper oxide, silver metal, silver oxide, samarium oxide and europium oxide.

6. A process in accordance with any of the preceding claims wherein said solution used in step (a) comprises at least one compound of Pt and at least one compound of at least one copromoter metal selected from the group consisting of Re, Fe, Ru, Cu, Ag, Sm and Eu, and said at least one compound of at least one copromoter metal is at least partially converted to at least one oxide of said at least one copromoter metal in step (b).
7. A process in accordance with any of the claims 1-5 further comprising the additional steps of:
 (a*) impregnating the material obtained in step (b) with a solution comprising at least one compound of at least one copromoter metal selected from the group consisting of Re, Fe, Ru, Cu, Ag, Sm and Eu, wherein said material obtained in step (b) comprises at least one substance selected from the group consisting of Pt metal and oxide of Pt; and
 (b*) heating the material obtained in step (a*) under such conditions as the substantially dry said material obtained in step (A*) and to at least partially convert said at least one compound of at least one copromoter metal to at least one oxide of said at least one copromoter metal;
 and wherein step (c) is carried out with the material obtained in step (b*).
8. A process in accordance with any of the preceding claims, wherein compounds of chromium, compounds of manganese and compounds of zinc are substantially absent in said composition of matter.
9. A process in accordance with claim 5, wherein said composition of matter contains about 0.2 to about 4 weight percent of said copromoter, expressed as metal.
10. A process in accordance with any of the preceding claims, wherein step (c) is carried out in a stream of H_2 at a temperature in the range of from about 350 to about 500 °C, for a period of time in the range of from about 0.5 to about 20 hours.
11. A process in accordance with any of the preceding claims, wherein said catalyst composition comprises from about 0.5 to about 5 weight percent Pt.
12. A process in accordance with any of the preceding claims, wherein said composition of matter comprises from about 0.5 to about 5 weight percent Pd.
13. A process in accordance with any of the preceding claims wherein said support material is used in step (a) has been extracted with an aqueous acidic solution, thereafter washed, dried and calcined.
14. A process in accordance with any of the claims 1 to 8, wherein said support material used in step (a) has been prepared by:
 (A) impregnating a porous ceramic material with a colloidal dispersion of titania in a suitable liquid dispersion medium, wherein dispersed silica is substantially absent in said colloidal dispersion;
 (B) heating the titania-coated material obtained in step (A) so as to obtain a substantially dried titania-coated porous ceramic material;
 and wherein said heating material obtained in step (c) in a reducing gas atmosphere is carried out at a temperature in the range of from about 0 to about 300 °C under such conditions as to activate said material obtained in step (b) and to form said composition of matter.
15. A process in accordance with claim 14, wherein step (c) is carried out in a stream of H_2 at a temperature in the range of from about 20 to about 200 °C, for a period of time in the range of from about 0.5 to about 20 hours.
16. A process in accordance with claim 14, wherein said colloidal dispersion used in step (A) contains titania particles having an average particle diameter in the range of from about 1 to about 100 nanometers, and said liquid dispersion medium is water.
17. A process in accordance with claim 14, wherein the colloidal dispersion used in step (A) comprises about 0.1-50 weight percent TiO_2 , and the TiO_2 -coated material obtained in step (B) contains about 1-40 weight percent TiO_2 .
18. A process in accordance with claim 14, wherein said porous ceramic material is monolith material, and said composition of matter comprises from about 0.5 to about 5 weight percent Pt, based on the weight of said catalyst composition excluding said monolith.
19. A process in accordance with claim 14, wherein said porous ceramic material is a monolith material, and said composition of matter comprises from about 0.5 to about 5 weight percent Pd, based on the weight of said composition matter excluding said monolith.
20. A process in accordance with claim 14, wherein said temperature in drying step (B) is in the range of from about 30 to about 200 °C.
21. A process in accordance with claims 18 or 19, wherein said composition of matter, excluding said monolith material, contains about 0.2 to about 4 weight percent of said copromoter, expressed as metal.
22. A composition of matter, from which silica is substantially absent and which is useful and effective as a catalyst for CO oxidation, comprising titania and at least one noble metal selected from the group consisting of platinum and palladium, prepared by a process of any of the claims 1 to 21.

23. A process for oxidizing carbon monoxide comprising the step of:
contacting a gas mixture comprising CO and O₂ with
a catalyst composition, from which silica is substantially absent, comprising titania and at least one noble
metal selected from the group consisting of platinum and palladium,
5 under such reaction conditions as to at least partially convert said CO and O₂ to CO₂;
wherein said catalyst composition is the composition of claim 22.
24. A process in accordance with claim 23, wherein said reaction conditions comprise a reaction
temperature in the range of from about -50 °C to about 400 °C, a reaction pressure in the range of from
about 1 to about 2,000 psia, and a volume ratio of CO to O₂ in the range of from about 1:100 to about
10 100:1.
25. A process in accordance with claim 23, wherein said reaction conditions comprise a temperature in
the range of from about -30 °C to about 170 °C, a reaction pressure in the range of from about 5 to about
20 psia, and a volume ratio of CO to O₂ in the range of from about 1:10 to about 10:1.
26. A process in accordance with claim 23, wherein said process is carried out in the cavity of a CO₂
15 laser so as to recombine CO and O₂ formed by dissociation of CO₂.

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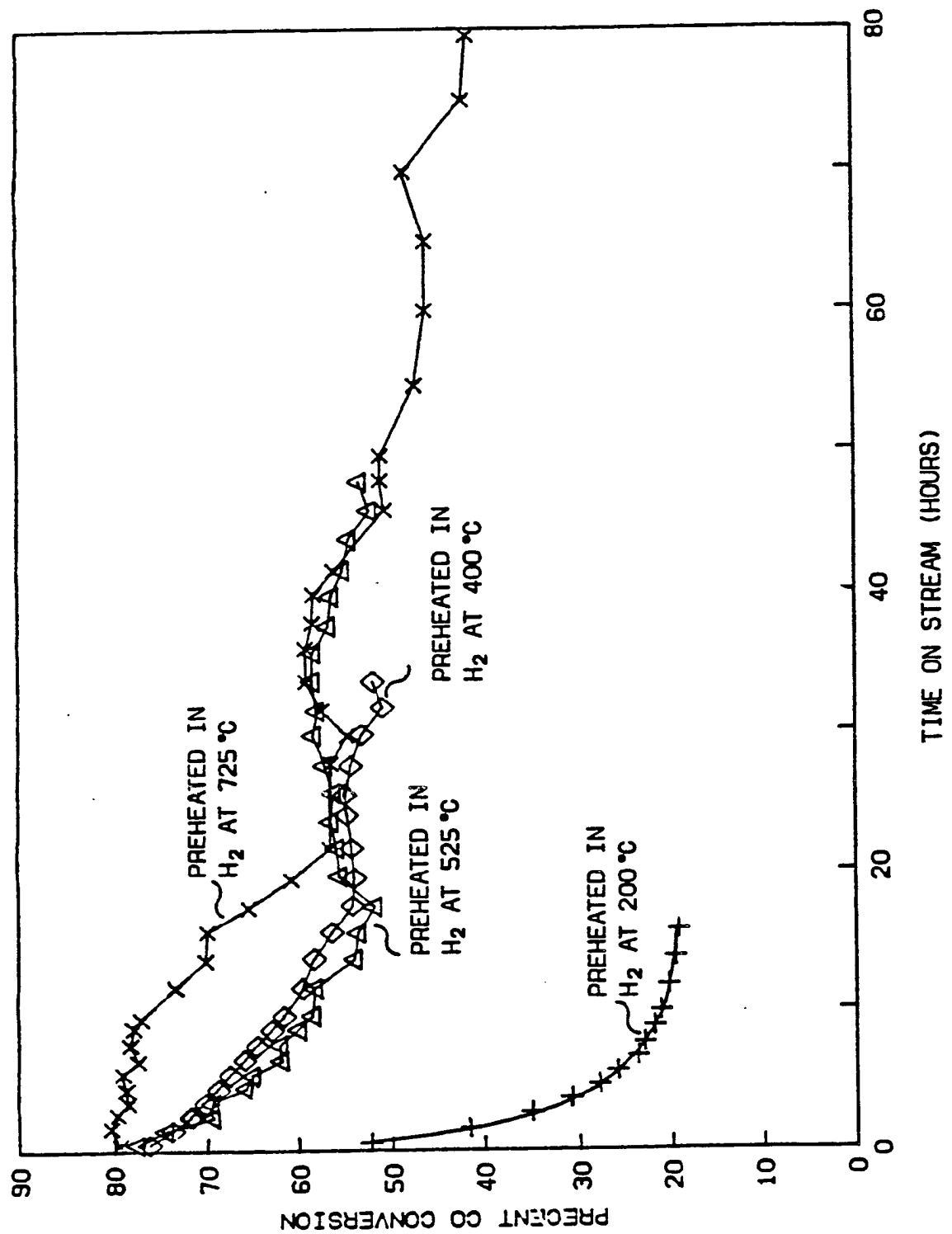


FIG. 1

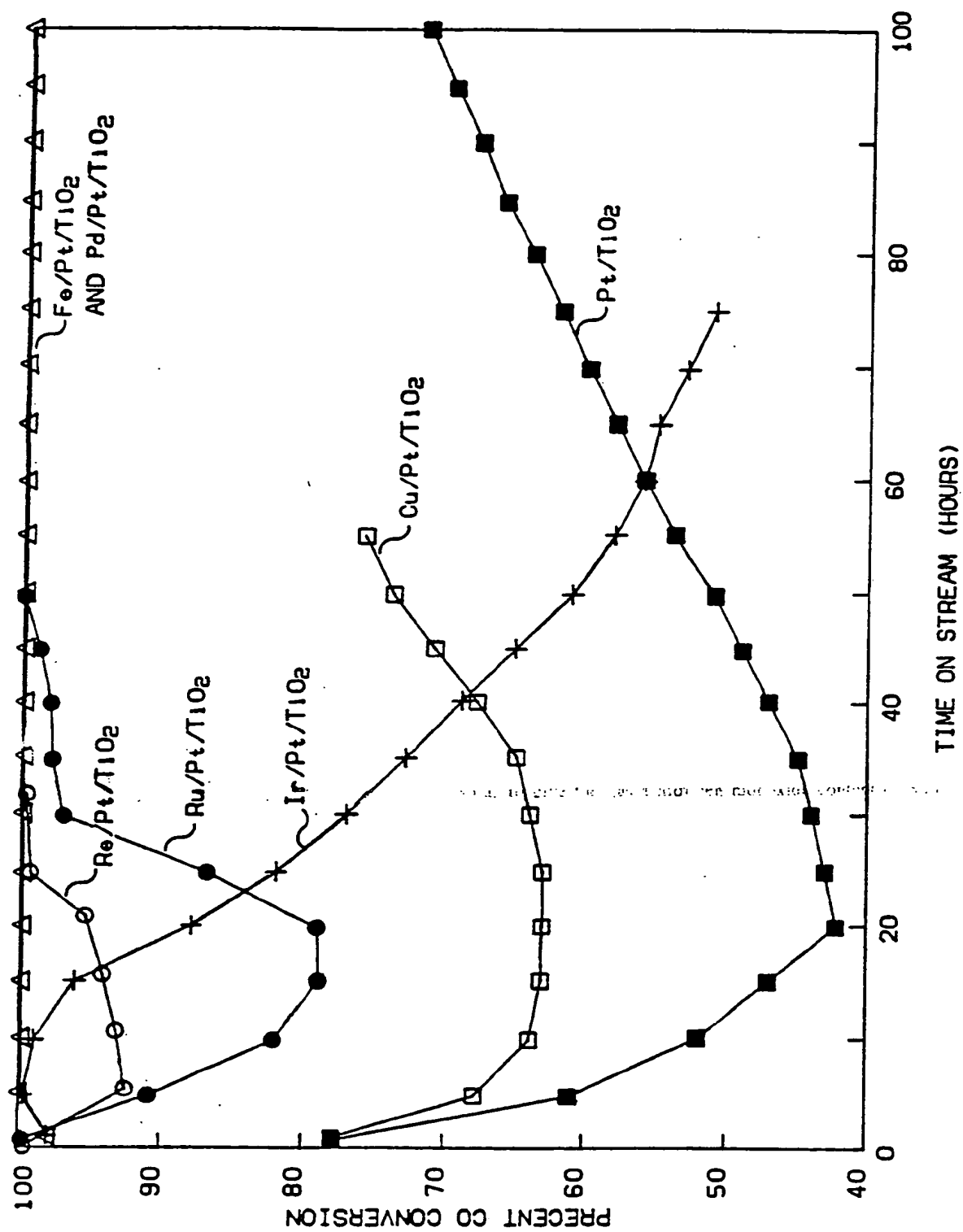


FIG. 2

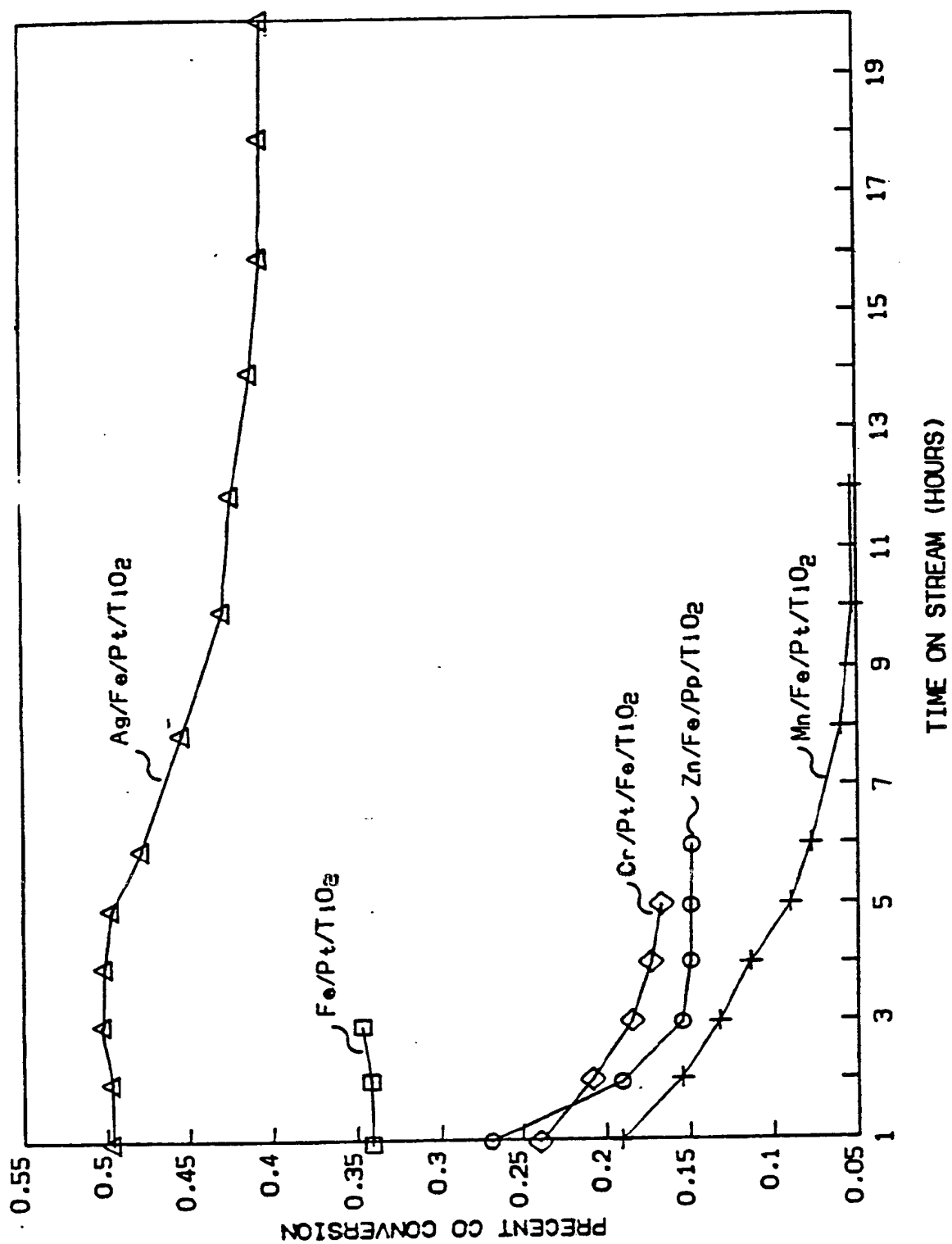


FIG. 3



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	US-A-4 537 873 (KATO et al.) * Abstract; column 2, lines 23-44; claims 1-18 * ---	1	B 01 J 23/40 B 01 J 37/18 B 01 J 23/89 H 01 S 3/03K
Y	US-A-4 499 205 (MASUDA) * Abstract; column 3, line 14 - column 4, line 46; claims 1-11 * ---	1	
A	US-A-3 023 173 (NIXON) ---		
D,A	US-A-4 639 432 (HALT et al.) ---		
D,A	US-A-3 963 827 (ACRES et al.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B 01 J H 01 S
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-11-1988	Examiner LO CONTE C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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